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METHOD FOR HYPERPOLARIZING ATOMIC NUCLEI AND A DEVICE FOR IMPLEMENTING THE METHOD.

CROSS REFERENCE TO RELATED APPLICATIONS

This application is the US national phase of PCT application PCT/DE2005/000023, filed 13 January 2005, published 28 July 2005 as WO 2005/069027, and claiming the priority of German patent application 102004002640.8 itself filed 19 January 2004 and German patent application 102004023345.4 itself filed 12 May 2004, whose entire disclosures are herewith incorporated by reference.

FIELD OF THE INVENTION

The invention relates to a method for hyperpolarizing atomic nuclei and a device for implementing the method.

BACKGROUND OF THE INVENTION

Recent developments in magnetic resonance tomography (MRT) and magnetic resonance spectroscopy (NMR) with polarized noble gases anticipate applications in medicine, physics and materials science. Polarization of noble gas nuclei may be achieved through optical pumping using alkali atoms, as described in the publication Happer, et al., Phys. Rev. A, 29, 3092 (1984).

The notion of optical pumping comprises the method developed by Kastler of significantly increasing by incident light radiation in material the occupation numbers of certain energy states relative to the state of equilibrium. By using optical pumping, the relative occupation numbers of the energy levels in atoms, ions, molecules and solid substances may be changed and ordering states induced. The occupation density of the optically

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pumped state differs noticeably from its thermal occupation probability according to the Boltzmann distribution. Through optical pumping of Zeeman levels, e.g parallel positioning of the magnetic moments of atoms and atomic nuclei may be obtained.

Typically, rubidium (an alkali atom) is used in practical operation in the presence of a noble gas and nitrogen making it possible to obtain a nuclear spin polarization of e.g ¹²⁹Xe of about 20 percent. Such a nuclear spin polarization is about 100,000 greater than the equilibrium polarization in clinical magnet resonance tomographs at 1 T and 300 K. The drastic increase of the signal-to-noise ratio explains why new application areas in medicine, science and technology can be expected in the future.

Polarization refers to the degree of orientation (ordering) of the spins of atomic nuclei or electrons. For instance, 100 percent polarization means that all nuclei or electrons are oriented likewise. Polarization of nuclei or electrons is tied to a magnetic moment.

Polarized xenon is, for instance, inhaled by or injected in a human being. 10 to 15 seconds later, the polarized xenon accumulates in the brain. The distribution of the noble gas in the brain is determined by using magnetic resonance tomography. The result is used for further analyses.

The choice of an noble gas depends in each case on its actual application. ¹²⁸Xe exhibits great chemical shift. If, for instance, xenon is adsorbed on a surface, its resonance frequency changes significantly. Moreover, xenon is soluble in lipophilic liquids. When such properties are desired, xenon is applied.

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The noble gas helium is hardly soluble in liquids. The isotope ³He is therefore regularly used when cavities are concerned. The human lung is an example of such a cavity.

Some noble gases have useful properties other that those mentioned above. For instance, the isotope ⁸³Kr, ²¹Ne and ¹³¹Xe have a quadrupole moment, of interest, e.g for experiments in basic research or in surface physics. However, these noble gases are very expensive, which makes them unsuitable for applications, in which greater amounts are used.

From the publication Driehuys, et al (Appl. Phys. Lett. (1996) 69, 1668) it is known how to polarize noble gases in a polarizer in the following way.

Based on a gas supply, a gas flow consisting of a mixture of $^{128}\mathrm{Xe}$, $^4\mathrm{He}$ and N_2 is enriched in a Rb container with Rb vapor and conducted through a pump cell. Using a laser, circular polarized light is produced, i.e., light in which the spin momentum or the spin of the photons exhibits the same direction. In the pump cell, the Rb atoms are optically pumped as an optically pumpable species with the laser beam ($\lambda\sim$ 795 nm, Rb Dl line) longitudinally to a magnetic field, thereby polarizing the electron spins of the Rb atoms. The spin momentum of the photons is thus transferred to free electrons of alkali atoms. The spins of the electrons of the alkali atoms thus vary greatly from thermal equilibrium, i.e., the alkali atoms are polarized. Through the collision of an alkali atom with an noble gas atom, the polarization of the electron spins is transferred to the noble gas atom, whereby polarized noble gas forms. The polarization of the electron spins of the alkali atoms

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created by optical pumping of alkali atoms is thus transferred through spin exchange of the alkali electron to the nuclear spin of the noble gases, as was first shown by Bouchiat with an Rb/3He system.

From Appelt et al (S. Appelt, A. Ben-Amar Baranga, C. J. Erickson, M. V. Romalis, A. R. Young, and W. Happer, Phys. Rev. A (1998), 58, 1412) regarding the theory of two-body collisions, it is known how to produce spin exchange between a pair of alkalimetal atoms.

From WO 99/08766 (US 6,318,092), it is known how to apply, besides an initial optically pumpable alkali metal, an auxiliary alkali metal as a non-optically pumpable species. The optically pumpable species thereby transfers the electron-spin polarization to the non-optically pumpable species, whereby effectively an increase of the polarization degree of the noble gas occurs.

Alkali atoms are used, since they possess a large optical moment of dipole, which interacts with light. Furthermore, each alkali atom exhibits a free electron, so that unfavorable interactions between two or more electrons per atom cannot occur.

Cesium would also be a well-suitable alkali atom, which is superior when compared to rubidium for obtaining the above-mentioned effect. However, there are no lasers currently available with a sufficiently high capacity, as is needed for the polarization of xenon by using cesium.

To use a maximum possible amount of photons, when employing broad-band high-performance semiconductor lasers, optical

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pumping of noble gases is done at pressures of several atmospheres. Optical pumping of alkali-metal atoms thereby differs according to the type of noble gas to be polarized.

In order to polarize ¹²⁸Xe, a gas mixture under a pressure of about 7 to 10 Bar is guided through a cylindrical glass cell continuously or semi-continuously. The gas mixture consists to 94 percent of 'He, to 5 percent of nitrogen and to 1 percent of xenon. The typical flow rate of the gas mixture is 1 cm per second.

In case of polarization of ³He, the required pressure in the polarizer is created by ³He itself, since the electron-spin relaxation rate of Rb-³He collisions is low. For Rb-¹²⁹Xe spin exchange pumps, this is not the case, which is why the pressure is created by an additional buffer gas such as ⁴He. The various relaxation and spin-exchange rates cause various requirements of the polarizers.

For ³He, the nuclear-spin polarization formation times are thus on the magnitude of hours. Since, however, the rubidium-spin destruction rate for rubidium ³He collisions is relatively low, operation at high ³He pressures (> 5 bar) is possible.

In contrast, for ¹²⁸Xe, the nuclear-spin polarization formation times based on the greater spin-exchange effective cross section are situated between 20 and 40 seconds. Based on the very large rubidium-electron spin-relaxation rate for rubidium-xenon collisions, the xenon partial pressure should only be less than 100 mbar for optical-spin-exchange pumps in order for a sufficiently high rubidium polarization to be maintained. That is why in such polarizers 'He is employed as buffer gas in order to achieve line

broadening.

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In a flow-through flow polarizer, the gas mixture initially flows through a vessel, referred to in the following as a "supply vessel," containing a certain amount of Rb. The supply vessel with the rubidium contained therein is heated together with the adjacent glass cell to about 100 to 150 degrees Celsius. By providing these temperatures, the rubidium vaporizes. The concentration of the vaporized rubidium atoms in the gas phase is determined by the temperature in the supply vessel. The gas flow carries the vaporized rubidium atoms from the supply vessel, e.g into a cylindrical optical pumping cell. A high-performance laser in continuous operation delivering circular polarized light with a capacity of about 100 Watt penetrates by radiation the optical pumping cell axially, i.e., in the direction of flow and optically pumps the rubidium atoms in a high-polarized state. The wavelength of the laser should thereby be adjusted to the optical absorption line of the rubidium atom (D1 line).

In other words, in order to optimally transfer the polarization of light to an alkali atom, the frequency of the light must match the resonance frequency of the optical transition.

The optical pumping cell is located in a static magnetic field B_{D} of about 10 Gauss created by coils, especially a so-called Helmholtz coil pair. The direction of the magnetic field runs parallel to the cylinder axis of the optical pumping cell or

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parallel to the direction of the laser beam, the magnetic field serving to guide the polarized atom. The rubidium atoms being optically highly polarized due to the light of the laser collide in the glass cell with the xenon atoms, among others, and release their polarization to the xenon-atoms.

At the exit of the optical pumping cell, rubidium deposits on the wall due to the high melting point compared to the melting points of the other gases. The polarized xenon or the residual gas mixture is passed along from the optical pumping cell and into a freezing unit consisting of a glass flask, whose end is submerged in liquid nitrogen. The glass flask is furthermore located in a magnetic field with a strength exceeding 1000 gauss. The highly polarized xenon gas deposits on the inner glass wall of the freezing unit as ice.

At the outlet of the cooling unit, the remaining gas ('He and N_2) is generally guided via a needle valve and finally released. The flow rate of the whole device may be controlled via the needle valve and a with measuring device.

If the flow rate increases too much, then there is no time for transferring the polarization from the rubidium atoms to the xenon atoms. Thus only minor polarization is obtained. If the flow rate is too low, then too much time will lapse before the desired amount of highly polarized xenon is frozen. Due to relaxation in the Xe ice, the polarization of the xenon atoms hence decreases. The relaxation of the xenon atoms is greatly delayed due the freezing, and also a strong magnetic field, which the cooling unit is exposed to. That is why it is necessary, following

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polarization, to freeze the noble gas xenon as quickly as possible and without loss. Relaxation through freezing cannot be entirely avoided.

However, at 77 K, one to two hours remain before the xenon polarization has decreased enough so that further application of the initially highly polarized gas no longer is possible.

A polarizer of the above-mentioned type always exhibits junctions. Junctions occur where at least two lines, through which polarized gas is guided, are connected with one another, whereby the lines usually consist of glass. The connection is established by a connecting element, such as flanges.

To polarize a single free alkali atom requires a certain energy. The required energy equals the resonance frequency for increasing the free electron of the alkali atom from a ground state to an excited state. In order to transfer the energy from a laser to the alkali atom in an optimal fashion, the frequency of the laser light should be adjusted to the resonance frequency of the alkali atom. Some lasers emit their light within a certain frequency spectrum. We are therefore not concerned with a single frequency, but a distribution of frequencies. The available laser spectrum is characterized by the so-called line width. In order to polarize alkali atoms commercially, broad-band semiconductor lasers are provided, whose frequency and line width are adjusted to the resonance frequency or the optical line width of the alkali atom.

In order to better transfer the energy from a laser to alkali atoms, collision partners for the alkali atoms are provided during polarization. As collision partners serve especially the

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'He atoms. Due to the interaction or collisions with the helium atoms, the optical line width of an alkali atoms expands. Increasing the width of this atomic spectrum makes it possible to use spectrally wide and therefore economical lasers.

The number of collisions between an alkali atom and a collision partner such as *He increases with increasing pressure. For 'He, for example, the expansion of the optical line width of the alkali atom is proportional to the pressure of the helium gas. In addition, *He has the value characteristic of only affecting slightly the polarization of the alkali atoms. For the polarization of '125 Xe, a gas mixture consisting to 94 Percent of 'He and with a pressure of about 10 bar is usually employed,.

The laser known from prior art with a power of 100 Watt for the hyperpolarization of the Rb electrons concerns a glass-fiber-coupled diode laser with a typical spectral width of 2 to 4 nanometers. With a gas pressure of 10 bar, the line width of the optical transition of rubidium atoms is expanded to about 0.3 nanometers. In the present rubidium-xenon polarizers, in which high-performance diode lasers with a typically 2-nanometer line width are applied for optical pumping, only a fraction of the laser light is therefore utilized.

The partial pressures of 'He are up to 10 bar in the gas mixture. This is very high compared with the other partial pressures (xenon or nitrogen), and is to ensure that polarized alkali metal or noble-gas atoms rarely reach the inner wall of the glass cell and lose their polarization there, e.g through interaction with paramagnetic centers. With increasing partial

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pressure of 'He, the probability that the polarized atoms collide disadvantageously with the inner wall of the cell decreases.

A polarized alkali atom, such as rubidium, is able to produce fluorescence radiation. If such radiation is captured by a further polarized alkali atom, depolarization of the alkali atom occurs. The nitrogen applied for the polarization of noble gases in the gas mixture serves to capture the fluorescence radiation in order to reduce the above-mentioned undesired depolarization. The nitrogen element in the gas mixture exhibits only a small partial pressure, as does similarly xenon. This partial pressure is typically about 0.1 bar.

The heavy noble-gas atoms, e.g xenon atoms, cause strong relaxation of the polarization of the alkali atoms when colliding with the alkali atoms. In order to maintain the polarization of the alkali atoms as high as possible during optical pumping, the partial pressure of the xenon gas in the gas mixture must be correspondingly small. Even with a xenon partial pressure in the gas mixture of 0.1 bar, laser capacities of around 100 Watt are required in order to obtain a polarization of the alkali atoms of about 70 percent in the whole test volume.

In prior art, optical pumping cells of glass blown from one piece are employed. This means that the windows, through which the laser light enters and exits, is always curved or rounded. During entry and exit of the laser light, undesirable and disadvantageous lens effects occur. The laser light is focused or widened, whereby the degree of polarization deteriorates considerably. The effective cross section of the optical pumping

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cell is therefore not uniformly illuminated by the laser light.

A gas volume with suitable composition is compressed according to prior art by a cylindrical optical pumping cell. The laser light producing the polarization is absorbed in the optical pumping cell. The pump beam thereby radiates through the optical pumping cell in the direction of flow of the mixture comprising the optically pumpable species and the atomic nucleus to be hyperpolarized parallel to the magnetic field.

U.S. patent 2002/0,107,439 Al discloses how laser light is radiated into a optical pumping cell against the current of a flowing mixture.

As a disadvantage, all previously known prior-art methods and devices for hyperpolarization provide only a comparatively low degree of polarization of the nuclear spins, at a maximum about 40%. The reason for this is interactions in the form of collisions of the alkali metal or noble gas against the inner walls of the optical pumping cell.

OBJECTS OF THE INVENTION

The object of the invention is therefore to make available a method for hyperpolarizing atomic nuclei and especially noble gas nuclei, which results in an increase of the degree of polarization.

A further object of the invention is to make available a device for implementing the method.

SUMMARY OF THE INVENTION

The method according to the invention provides for the transfer of a polarization created by a laser of an electron spin

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of an optically pumpable species in a mixture onto the nuclear spin of an atom to be hyperpolarized. The mixture comprises the optically pumpable species, the nuclei to be polarized and possibly further components, such as buffer and quench gases, as well as possibly a further alkali metal type as an auxiliary alkali metal.

The components of the mixture or other inert components for hyperpolarization are fed by means of a suitable design of the inlet of the optical pumping cell for these components in such a way that the optically pumpable species and/or nuclei to be hyperpolarized do not come in contact with the inner walls of the optical pumping cell, or only slightly. This prevents unfavorable interactions in the form of collisions of the alkali metals and/or the noble gas against the inner walls of the optical pumping cell, which otherwise would reduce polarization of the electrons of the optically pumpable species and the nuclei to be hyperpolarized along the effective cross section of the optical pumping cell.

As an advantage, it is possible for the hyperpolarization of inert compounds, to feed buffer gases to the optical pumping cell in such a way that the relaxation of the optically pumpable species and that of the atomic nuclei to be hyperpolarized is avoided through collisions at the inner wall.

The mixture with optically pumpable species and nuclei to be hyperpolarized may, however, also itself be fed as a jet flow cell into a optical pumping cell. The jet flow cell comprises the mixture. Its components do not touch the inner walls of the optical pumping cell due to its embodiment in the form of a jet flow cell. This measure alone causes the optically pumpable

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species and/or the nuclei to be hyperpolarized not to touch the inner walls of the optical pumping cell.

Depending on the gas pressure and the flow rate of the mixture, the jet flow cell and/or the bypass flow is formed and fed into the optical pumping cell in such a way that the lingering period of the hyperpolarized optically pumpable species and that of the hyperpolarized nuclei in the optical pumping cell is lower than the time for their diffusion up to the inner walls of the optical pumping cell.

The formation of the bypass flow and/or jet flow cell thus entails that the mixture with the hyperpolarized optically pumpable species and the hyperpolarized nuclei can only touch the inner walls at the position at which the mixture is guided out again from the optical pumping cell for the purpose of enrichment.

Relaxation of the optically pumpable species and/or the hyperpolarized nuclei due to collisions at the inner walls of the optical pumping cell is thus complete obviated.

The jet flow cell may be formed as a thin layer with a thickness of e.g 1 cm and/or possibly less than 1 cm diameter.

The mixture will then be injected as a jet flow cell in the optical pumping cell and does not touch its inner walls, or only to a much lesser extent as is the case according to prior art by simply pressing the mixture through a optical pumping cell. No convection currents appear at the inner walls. The flow rate of a volume element is, e.g about 0.5 cm per second and the pressure in the optical pumping cell. e.g 7- 15 bar.

In addition, the device according to the invention

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features means for injecting the mixture into the optical pumping cell as a jet flow cell, so that the mixture will not collide with the walls, whereby wall relaxation is avoided. Such a flow polarizer will be referred to as a jet polarizer in the following.

A nozzle may be provided as a means for forming the jet flow cell. The nozzle is connected with the gas supply of the optical pumping cell and exhibits dimensions capable of forming a jet flow cell of the mixture. Moreover, the gas mixture is injected with an appropriate pressure via the nozzle in the optical pumping cell.

An especially simple and effective optical pumping cell with reduced wall relaxation relative to prior art provides for inclining the inlet and/or outlet connection(s) with a defined angle, rather than using a 90° angle (relative to the longitudinal axis of the cell).

A gas supply comprises the lines and the storage tanks for a certain species, such as the optically pumpable species and other inert components, as well as for the nuclei to be hyperpolarized. Several gas supplies deliver the various gases that are needed for the hyperpolarization of a certain type of nuclei or noble gases. Mixing chambers for mixing the various components may be provided.

The components of the jet flow cell injected in the optical pumping cell through the nozzle do not touch the walls, so that a wall relaxation of the optically pumpable species and the hyperpolarized nuclei is avoided. In effect, the formation of the jet flow cell by the device according to the invention causes a

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rise in the degree of polarization, when implementing the methods.

The method is, moreover, implemented such that the distance between the end of the jet flow cell, at which the mixture is guided out of the optical pumping cell, and the laser-light inlet window(s) is chosen sufficiently large so that the components of the mixture, especially the optically pumpable species cannot settle on the inner walls of the laser-light inlet window(s).

This measure, in itself, also causes a clear increase of the polarization of the hyperpolarized atom nuclei.

The laser-light inlet window of the optical pumping cell may in addition exhibit a maximum distance to the inlet of the optical pumping cell for the optically pumpable species.

The thickness of the optically pumpable species may thus be chosen very large, e.g at least $10^{14}~\rm cm^{-3}$ *SRb atoms and above, without causing the so-called unfavorable effects of the optically pumpable species settling at the laser-light inlet window(s).

Within the scope of the invention, it was realized that for prior-art polarizers with in- and outlets for the mixture at a right angle to one side wall of the cylindrical optical pumping cell, a thin layer of the optically pumpable species settles over time at the inner surface of the laser-light inlet window due to the spatial proximity to the inlet for the mixture, which layer when exposed to a pump beam with high power intensity evaporates while a boundary layer < 0,3 mm) of great thickness forms. Since the atoms in this boundary layer are almost non-polarized, a large proportion of the performance of the pump beam is absorbed in this boundary layer (> 50 %). This performance absorbed in the boundary

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layer is no longer available for the actual pumping process in the cell. Moreover, the strong temperature gradient according to prior art appearing between this boundary layer and the other cell volume stimulates convective currents in the cell. This causes the transport of the gas at the cell walls to accelerate and wall relaxation to increase further. Moreover, wall relaxation of the nuclear spins is increased dramatically due to the contact with the boundary layer. The flow of the mixture according to prior art thus occurs in a U-shaped fashion.

The method according to the invention may also be implemented such that the bypass flow consisting of an inert compound is guided into the optical pumping cell in order to separate the mixture from the inner walls.

The inlet window(s) for the laser(s) is/are rinsed with a bypass flow. The bypass flow is guided into the optical pumping cell such that it encloses the jet flow cell and rinses the inner walls of the optical pumping cell. The bypass flow has no adverse effects relative to the hyperpolarization.

The bypass flow comprises advantageously an inert compound, which is needed for the hyperpolarization of a certain nucleus. As an example, a bypass flow consisting of 'He for the hyperpolarization of 12°Xe may be mentioned.

The bypass flow is created by means comprising, e.g a nozzle and at least one separate gas supply connected therewith, with which a thin bypass flow for rinsing the inner walls of the optical pumping cell is created and guided thereinto. This will cause the mixture in the jet flow cell not to collide with the

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walls. Wall relaxation of the optically pumpable species and the nuclei is thus prevented.

The laser may, especially in case of a cylindrical optical pumping cell, be arranged such that the laser light in a counter current, i.e., antiparallel to the direction of flow of the mixture flowing in the optical pumping cell and the magnetic field, will produce a further Increase of the degree of polarization of the nuclear spins of the mixture exiting the cell versus a flow polarizer with a direction of radiation of the laser lights with or against the direction of flow the mixture. [A redundant particle seems to upset the meaning of this sentence or something was left out!]

In a further especially advantageous embodiment of the invention, the walls of the optical pumping cell are cooled during the process. Moreover, the device may comprise, e.g a thermo box. A device comprising means for cooling the walls differ from the previous devices, such as flow polarizers, in which the walls always are heated at the same time. This is possible due to separate heating for the components of the mixture before the inlet of the optical pumping cell and the formed jet flow cell, since the latter [?] causes prevention of wall contact of the optically pumped gases during transit time.

This measure advantageously optimizes heat removal from the gas mixture. A further especial advantage is that nonpolarized atoms such as alkali metals are not released from the inner walls.

In a further embodiment of the invention, the spin

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exchange during the process is transferred indirectly to the nuclear spin of a nucleus to be hyperpolarized. The spin exchange is thereby initially transferred from the electrons of an optically pumpable species to the electrons of at least one species that is not optically pumpable by the laser(s) and from there transferred to the nuclei of the nuclei [sic] to be hyperpolarized. The laser light does not pump the non-optically pumpable species. Then, a greater thickness of the non-optically pumpable species versus the optically pumpable species is advantageously selected. A further advantageous result is that non-optically pumpable species exhibiting a high efficiency, especially an efficiency close to 1, may be selected for the transfer of the electron spin polarization to the nuclear spin.

The hyperpolarization device comprises for this purpose at least two storage containers for the optically pumpable species and the non-optically pumpable species, whereby these are also used for indirect spin-exchange optical pumping. The storage containers are each advantageously arranged in a separate gas supply for the device and provided with their own heating.

The device is furthermore designed such that the laserlight inlet window of the optical pumping cell exhibits a maximum distance to the inlet of the optical pumping cell for the optically pumpable species. The advantageous result is that the optically pumpable species will not settle at the inlet window.

The laser-light inlet window of the optical pumping cell may especially advantageously exhibit a distance to the exit of the optical pumping cell for the mixture that is large enough to

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prevent settling of the optically pumpable species on the inner wall of the laser-light inlet windows. Through suction ducts and lines, the mixture is sucked off radially to the optical pumping cell. We are thus concerned with a flow-through polarizer.

The formation of a bypass flows, a jet flow cell, the above-mentioned minimum distances of the mixture from the inner walls depending on flow rate and pressure, as well as appropriate laser devices, each on their own result in the avoidance of interaction of the mixture with the inner walls of the optical pumping cell and an increase in the degree of polarization during the process. In combination with one another, a further increase of the degree of polarization of the nuclei to be polarization may be obtained.

The coils for creating a magnetic field are arranged such that the direction of the magnetic field is against or in the direction of the laser beam

As optically pumpable and possibly non-optically pumpable species, especially alkali metals are selected, since they exhibit a great moment of dipole.

The method according to the invention is especially suited, e.g for hyperpolarizing ¹²⁹Xe by using ⁸⁵Rb alone, or by using ^{a5}Rb as an optically pumpable and a cesium isotope as non-optically pumpable species. However, it may also be hyperpolarized using ⁸⁵Rb and/or the cesium isotope, or even ¹³CO₂.

The mixture is guided through the flow-through polarizer, either continuously or semi-continuously. In case of ${}^{3}\text{He}$, a polarizer with closed optical pumping cell is used.